云 南 植 物 研 究 2000,22(1):116~118
Acta Botanica Yunnanica

滇姜花中的新二萜成分—滇姜花戊素*

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摘要:从滇姜花根茎中分离到1个新二萜成分,命名为滇姜花戊素(1),其结构经波谱学方法鉴定为13β-furanolabda-8(17),11-dien-6β,7α-diol。

关键词:滇姜花,滇姜花素E;二萜
中图分类号:Q 946 **文献标识码**:A **文章编号**:0253-2700(2000)01-0116-03

Yunnancoronarin, a New Diterpenoid from *Hedychium yunnanense*

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Abstract: A new diterpenoid named yunnancoronarin E(1), was isolated from the rhizomes of *Hedychium yunnanense* Gagnep. Its structure was elucidated as 13β-furanolabda-8(17),11-dien-6β,7α-diol by spectra methods.

Key words: *Hedychium yunnanense*; Yunnancoronarin E, Diterpenoid

We reported series of antitumor diterpenoids from plants of *Hedychium yunnanense* (Zhao *et al*, 1995a; Zhao *et al*, 1995b; Zhao *et al*, 1996) and *H. forrestii* (Zhao *et al*, 1995c). Further study on the rhizomes of *Hedychium yunnanense* resulted in the isolation of one labdane type diterpenoid. In this paper we describe the structural elucidation of this compound.

Results and Discussion

Dried and pulverized rhizomes of *Hedychium yunnanens* collected in Guandu District, Kunming, China, in 1993, were extracted with alcohol three times. The extract was further extracted whith petroleum ether three times to give brown oil. Brown oil was purified by repeated column

* Foundation item: Program granted by the Laboratory of Phytochemistry, Kunming Institute of Botany, the Chinese Academy of Sciences.
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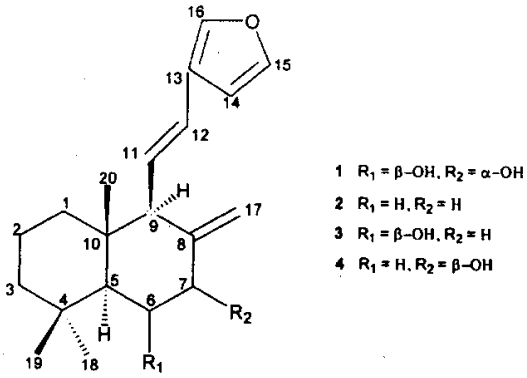
Received date: 1999-05-19, Accepted date: 1999-07-08

chromatography on silica gel and alumina to afford 1.

Compound 1, colorless oil, its molecular formula was determined to be $C_{20}H_{28}O_3$ by HRMS. The IR spectrum suggested the presence of hydroxyl group(3452 cm^{-1}), gem dimethyl (1387, 1377, 1263 and 1160 cm^{-1}) and a furan (1509, 871 and 775 cm^{-1}). The ^{13}C NMR spectrum gave 20 carbon signals, including eight olefinic carbons ($C \times 2$, $CH \times 5$, $CH_2 \times 1$), and twelve saturated carbons ($C \times 2$, $CH \times 4$, $CH_2 \times 3$, $CH_3 \times 3$), The ^1H NMR spectrum indicated the presence of an unsaturated methlene group, and trans double bond, and a β－substituted furan ring, three mthyl group.

The ^{13}C and ^1H NMR spectra of **1** were similar to those of coronarin E(**2**), yunnancoronarin (**3**) (Zhao *et al*, 1995a), and coronarin A(**4**) (Zhao *et al*, 1995c) indicating **1** was a labdane type furanoid diterpene. Comparision of ^{13}C NMR spectra of **1** and **2 ~ 4** suggested that both of C－6 and C－7 of **1** were substituted by hydroxyl groups. The complete ^1H and ^{13}C NMR assignments were deduced from the $^1H-{}^1H$ cosy and $^{13}C-{}^1H$ cosy spectra. Orientations of 6－OH and 7－OH were determined by NOESY spectrum(see Figure1)：NOE observed between H－5 and H－6 suggested that H－6 is equatorial orientation, and NOE displayed between H－7 and H－17 a indicated that H－7 is equatorial orientation, and there fore both 6－OH and 7－OH were axial orientation. The above conclusion can also be supported by comparation of NMR data of **1** with those of **2** and **4**；：downfield shift of H－19, 20 and downfield shift of C－19, 20 due to 1,3－diaxial interactions of 6β－OH, while downfield shift of H－5, 9 and upfield shift of C－5, 9 due to γ－gauche effect of 7α－OH. Thus, the structure of (**1**) was elucidated to be 13β－furanolabda－8(17), 11－dien－6β, 7α－diol.



1 R_1 = β-OH, R_2 = α-OH
2 R_1 = H, R_2 = H
3 R_1 = β-OH, R_2 = H
4 R_1 = H, R_2 = β-OH

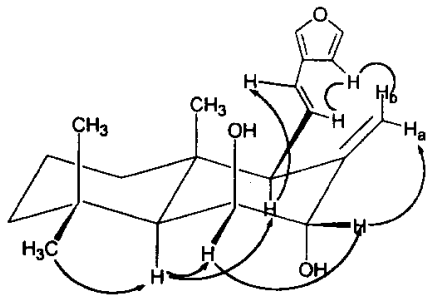


Fig. 1 Key NOE relationships for 1

Experimental

General Mps. uncorr. Optical rotations were recorded on SEPA－300 with 2 cm cell. IR were taken with Perkin－Elmer 577. NMR were measured with AM－400 spectrometer using TMS as the internal standard. MS were determined with VG Autospec－3000 mass spectrometer.

Extraction and isolation The dried and pulverized rhizomes of *Hedychium yunnanens* (4.0 kg)

collected in Guandu District, Kunming, China in 1993, were extracted with 95% EtOH three times at refluex condition. The EtOH extracts (410g) was extracted with petroleum ether three times. Then the petroleum ether solutions were evaporated and got brown oil (230g). The brown oil was separated into six fractions (Fr. A ~ F) by subjecting it to silica gel column chromatography (CC) using a ptroleum ether – EtOAc gradient system. Fr. D was subjected to silica gel column chromatograply eluting with petroleum ether – acetone (4 ∶1), silica gel column chromatography eluting with petroleum ether – EtOAc (4 ∶1), alumina column chromatography eluting with $CHCl_3$ – EtOAc(4 ∶1) to afford 12 mg of **1**.

Yunnancoronarin E(1) $C_{20}H_{28}O_3$, colorless oil, $[\alpha]_D^{20}$ – 18.57°(c 0.175, $CHCl_3$). IR ν_{max}^{KBr} (cm^{-1}) ∶3452, 2924, 2853, 1509, 1387, 1377, 1263, 1160, 871, 775, EIMS m/z(rel. int.) ∶316[M]$^+$(17), 298(5), 153(25), 133(36), 105(53), 91(65), 77(69), 69(72), 55(100); HRMS ∶found ∶m/z ∶317.208 $[M+1]^+$, $C_{20}H_{29}O_3$ requires ;317.2117 ;^{1}H NMR($CDCl_3$, δ); 7.35(1H, s, H – 16), 7.34(1H, s, H – 15), 6.53(1H, s, H – 14), 6.25(1H, d, J = 15.6 Hz, H – 12), 5.96(1H, dd, J = 15.6, 9.9 Hz, H – 11), 5.16(1H, s, H – 17a), 4.92(1H, s, H – 17b), 4.23(1H, br.s, H – 6), 4.11(1H, d, J = 2.4 Hz, H – 7), 2.92(1H, d, J = 9.9 Hz, H – 9), 1.55(1H, br.s H – 5), 1.22(1H, s, H – 19), 1.12(1H, s, H – 20), 1.02(1H, s, H – 18). ^{13}C NMR($CDCl_3$, δ) ∶43.5(t, C – 1), 19.3(t, C – 2), 44.2(t, C – 3), 34.1(s, C – 4), 50.6(d, C – 5), 72.8(d, C – 6), 78.5(d, C – 7), 148.4(s, C – 8), 55.8(d, C – 9), 40.2(s, C – 10), 122.7(d, C – 11), 126.6(d, C – 12), 124.3(s, C – 13), 107.6(d, C – 14), 139.8 (d, C – 15), 143.4(d, C – 16), 115.0(t, C – 17), 33.4(q, C – 18), 24.6(q, C – 19), 17.7 (q, C – 20).

References

Zhao Q, Hao X J, Chen Y Z *et al*, 1995a. Studies on diterpenoid constituents of *Hedychium yunnanense*[J]. *Chemical Journal of Chinese Universities*(**高校化学学报**), **16**(1) ∶64 ~ 68

Zhao Q, Hao X J, Chen Y Z *et al*, 1995b. Sesquiterpenoids from *Hedychium yunnanense*[J]. *Acta Botanica Yunnan*(**云南植物研究**), **17**(2) ∶201 ~ 203

Zhao Q, Hao X J, Chen Y Z *et al*, 1995c. Studies on diterpenoids from *Hdychium yunnanense* and their antitumor activity[J]. *Acta Pharmaceutica Sinica*(**药学学报**), **30** ∶(2)119 ~ 122

Zhao Q, Hao X J, Chen Y Z *et al*, 1996. Studies on photosensitized oxidation of diterpenoids from *Hedychium* genus[J]. *Chinese Chemical Letters*(**中国化学快报**), **7**(1) ∶25 ~ 28